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October 10, 1994
SP307:101094:03

Mr. Andy Ledford
EG&G Rocky Flats, Inc.
Rocky Flats Environmental Technology Site
P.O. Box 464, Building 080
Golden, Colorado 80402-0464

Subject: MTS 343756 GG
OU4 Solar Ponds IM/IRA
Submittal of Predicted OU4 K_d Values for IM/IRA Modeling

Dear Mr. Ledford:

Enclosed are the proposed testing methodologies for use with the VD2ST modeling. In addition, ES has provided the predicted K_d values that will be used for the preliminary modeling that is currently underway. Please forward this information to your colleague Mr. Tom Boeckman for consideration by Haliburton/NUS.

Please call me at 764-8811 or pager 687-2551 if you have any questions.

Sincerely,

Philip A. Nixon
Project Manager: Solar Pond IM/IRA

cc:

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3.0 LABORATORY TESTING

3.1 PHYSICAL PROPERTIES DETERMINATIONS

It is proposed that laboratory determinations of all of the following physical parameters be made on representative samples of each physically distinct material mixture anticipated for inclusion beneath the engineered cover (see section 3.2 below for description of samples):

1) Porosity
Using a standard calculation method (Klute, 1986, Chap. 18, pp. 444-445), porosity is calculated from:
1. <u>bulk (dry) density</u> (Klute, 1986, Chap. 13, 364-367)
2. <u>particle density</u> (ASTM D-854-91)

2) <u>Saturated hydraulic conductivity</u> (Klute, 1986, Chap. 28, pp. 700-703)

3) <u>Soil water (moisture) content</u> ASTM D2216-90

4) <u>Moisture retention characteristic curves</u> (Klute, 1986, Chap. 26, 637-639 and 644-649)

5) <u>Sieve analysis</u> ASTM D-422-63 (90)

3.2 CHEMICAL PROPERTIES DETERMINATIONS

It is proposed that laboratory determinations of desorption-mode partition coefficients be made on all materials anticipated for inclusion beneath the IM/IRA engineered cover. To simplify the laboratory procedure, all tests will conducted as batch tests.
A description of the materials to be tested and their sources follows:

1) Four samples of SEP-proximal, contaminated, unconsolidated vadose zone material (three different and one duplicate). Soil samples would be retrieved from existing cores obtained during RF/RFI Phase I investigations and selected on the basis of physical properties (eg., soil moisture characteristic curves) and contamination levels. The selection process would attempt to identify a) samples representative of the range of soil types present in the vicinity of SEPs and b) soils with optimal contaminant concentrations (i.e., relatively high) for laboratory batch desorption experiments. Approximately 1 kg of selected intervals will receive radiological screening and be shipped to the selected testing laboratory.

2) Mixture(s) of soil, sludge and chemically-fixed sludge moisture. This is the recently proposed waste form now being considered by HNUS). This mixture will be prepared by HNUS using OU4 unconsolidated vadose material in the form of drill cuttings (the "soil", retrieved from storage drums) and the

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sludge/chemically fixed sludge water solid mixture designed by HNUS. All components will be mixed in the proportions anticipated for the final IM/IRA structure. If more than one candidate recipe for the mixture is designed by HNUS, a sample of each mixture should be tested. A 1 kg sample of each mixture will be shipped to the selected testing laboratory.

3) Mixture(s) of soil and pondcrete. This mixture will be prepared from soils (as described in 2) above) and existing pondcrete. The mixture will simulate the proportions and final pondcrete aggregate size anticipated for the final IM/IRA structure. If more than one candidate recipe for the mixture is designed, a sample of each mixture should be tested. A 1 kg sample of each mixture will be shipped to the selected testing laboratory.

4) Mixture(s) of soil and asphaltic pond liners. This mixture will be prepared from soils (as described in 2) above) and representative samples of pond liners. The availability of pond liners is currently in question and should be discussed.

The experimental design will be developed in cooperation with the selected analytical laboratory with the objective of simulating, as closely as possible, the conditions expected beneath the IM/IRA engineered cover. In addition the requirements of trace metal and radiochemical analyses will be considered. The following design criteria will be used:

1) All tests will be conducted in a desorption-mode. Since the conceptual model for long-term performance of IM/IRA wastes includes contact of wastes with clean (initially meteoric) water with subsequent transfer of contaminants to the liquid phase, soil samples will be mixed with clean (contaminant-free) water. This contrasts with the far more commonly performed adsorption-mode experiments in which contaminants are initially placed in the liquid phase and equilibrated with clean soils.

2) Existing ("native") levels of contamination will be used, i.e., no contamination will be added (spiked) to the soil. This procedure assures that the desorption-mode partitioning of contaminants will occur under actual field conditions rather than those of artificially highly contaminated soils.

3) Existing cores will be brought back to original soil moisture levels by the addition of pure water and homogenized. Since some highly soluble contaminants (e.g., nitrate) are expected to exist in vadose zone soils principally as solutes in soil moisture, an attempt to replicate the original conditions will be made.

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4) Homogenized, rehydrated soils will be analyzed for all contaminants of concern prior to experimentation. The RF/RFI Phase I practice of analyzing a six foot interval aggregate of core will not provide adequate data for calculating partitioning coefficients.

5) Soil/water ratios will be estimated on the basis of starting soil concentrations and conservative (high) estimates of K_d values so as to achieve 10x MDL concentrations in the liquid phase. This will assure the greatest likelihood of obtaining liquids with sufficient contaminant concentrations to be analyzed.

6) Liquid volumes will be sufficiently large (2000 to 2500 ml) to allow adequate concentrations of radionuclides for standard counting procedures. Smaller volumes will force laboratories to extend counting times and increase minimum detection limits.

7) Batch tests will be performed in an NBS rotary extractor to assure comparability with other data (Roy et al., 1991)

8) Equilibration times will be no less than 24 hours (Roy et al., 1991).

9) Equilibrated batch slurries will be allowed to settle and the solutions will be decanted and filtered through a 0.1 μm filter.

10) All filtered equilibrated solutions will be analyzed for all contaminants-of-concern, pH, TDS and a full suite of water quality parameters. Contaminants-of-concern and desired minimum detection limits (MDL) are listed in Table 1 and discussed in the explanation of Table 1.

11) All filter membranes will be analyzed by radiochemical methods to detect the possibility of suspended-matter associated contaminants.

12) All batch procedures will be repeated on the same solid mass to establish trends in partitioning. Ideally, K_d values would be identical for successive batch experiments (as long as K_ds are relatively high and contaminant concentrations in the solid material are not limiting - i.e., so small that the contaminant is completely removed). It is very possible that initial batch runs will be atypical of (lower than) successive runs because of anomalous initial dissolution or particulate releases. K_d values may thus only be indicative of initial mobility of contaminants in the IM/IRA structure and could over-estimate long-term mobility. It is proposed that batch experiments be repeated until some level of consistency (repeatability) is obtained.

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TABLE 1 Prediction of Leach Test Parameters and Feasibility

Analyte	Analytical Method (a)	Required Liquid Volume (L) (b)	Analytical Minimum Detection Limit (MDL) water/soil pCi/L / pCi/g (c)	Assumed Initial Soil Concentration (d)	Assumed "Conservative" Partition Coefficient ml/g or L/Kg (e)	Maximum resolvable K_d at 10 X MDL (and MDL) with 500 g Soil (f)
Am-241	α-spec.	2.5	0.01/0.02	0.6 pCi/g	50000[1]	5000 (60000)
Cs-137	γ-spec.		1/.5	0.3 pCi/g	5000[4]	30 (300) *
Pu 239/240	α-spec.	2.5	0.01/0.03	2.5 pCi/g	5000[2]	20000 (100000+)
Ra-226	Rn-emanation	1	0.5/0.5	0.7 pCi/g	5000[5]	150 (1500) *
U 233/234	α-spectrometry	2.5	0.6/0.3	2 pCi/g	1000[3]	300 (3000)
U-235	α-spectrometry	2.5	0.6/0.3	0.1 pCi/g	1000[3]	10 (100) *
U-238	α-spectrometry	2.5	0.6/0.3	1 pCi/g	1000[3]	1700 (1700)
Be	ICP spec.	0.1	0.0003 mg/L	1 mg/Kg	2000[7]	300 (3000)
Cd	ICP spec.	0.1	0.004 mg/L	55 mg/Kg	1000[6]	1500 (15000)

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Explanation to accompany Table 1.

(a) Analytical methods

Am-241	0.01 pCi/L †
Cs-134	§
Cs-137	§
Pu-239/240	0.01 pCi/L †
Ra-226	§
Sr-89	§
Sr-90	§
U-233-234 *	0.6 pCi/L †
U-235 *	0.6 pCi/L †
U-238 *	0.6 pCi/L †
Cd #	0.005 mg/L
Be #	0.0003 mg/L

* Although total uranium should be sufficient, isotopic determinations improve sensitivity and is consistent with existing analytical protocol.

Cd and Be appear to be the only metal of concern, a multi-element ICP analysis would be appropriate.

† Isotopic analyses by microprecipitation or electrodeposition followed by alpha spectrometry. Detection limits were supplied by Karen Schoendahler, EG&G and represent contract detection limits

§ Feasibility of determining these analytes is dependent on exact analytical scheme (to be determined) because of volume requirements.

(b) 2.5 L is given for all α-spectrometry determinations for maximum sensitivity and reproducibility as well as minimum counting time.

(c) For all radiometric determinations the detection limits are taken from the GRASP

(d) Assumed initial soil concentrations (or activities) are based on OU4 Phase I RFI/FS analyses of vadose-zone borehole soils. <u>The selection of soil samples from existing material (eg/ remaining core, cuttings etc.), so as to obtain the maximum contaminant levels, is critical to the success of the leach tests where high K_d values are expected</u>. As can be seen from the attached figures, the activity of ^{241}Am in the liquid is quite sensitive to the initial activity of ^{241}Am in the soil. This limitation can not be circumvented by including more soil in the test chamber as the liquid activity is very <u>in</u>sensitive to soil mass at high K_ds.

Given that there is no assurance that residuals of those

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samples having maximum concentrations will still be available or that the maximum concentrations will be reproducible, the assumed starting soil concentration or activity is taken to be one-tenth of the maximum reported value.

(e) Kd values (stated as ml/g) listed in this column represent "conservative" (with respect to the experimental design, not with respect to environmental protectiveness) estimates taken from the literature, i.e., they are among the highest values. An experimental soil:water ratio, based on a high estimated Kd, that produces a sufficiently large liquid-phase analyte concentration for analytical purposes will also be adequate if the Kd turns out to be lower - hence, it is a "conservative" estimate.

(1) *Americium* Thibault et al. (1990) suggest an average Kd = 9600 for silt soils but more credible estimates give lower and higher values: 100 (Looney et al., 1987); up to 43000 (Ames and Rai, 1978). K_d = 50000 is considered completely conservative. However, for K_ds = 50000 ^{241}Am would be expected to be present at the detection limit of 0.1 pCi/L and only for K_ds < 5000 would ^{241}Am activities be > 10X MDL.

(2) *Plutonium* Thibault et al. (1990) suggest a geometric mean K_d = 5100, Looney et al., (1987) recommends 100, and Miner et al., (1982) gives a range of 43 to 2700 for Rocky Flats soils.

(3) *Uranium* Although Thibault et al. (1990) suggests a mean K_d value of 1600 for clay soils, their values for other soil types are significantly lower (35 for sand soils and 15 for silt soils). Additionally, other authors consistently list lower values for uranium: Looney et al. (1987) recommends 39 and Ames and Rai (1978) give 270 for clay-rich soils without $CaCO_3$ and as low as 16 for clay with $CaCO_3$. A value of 1000 is considered to be sufficiently conservative. For the soil masses given in Table 1, ^{233}U and ^{238}U are not likely to present an analytical problem but ^{235}U will be near detection levels for a K_d = 1000 even for a 1000 g soil sample in 2.5 L.

(4) *Cesium* Thibault et al. (1990) gives 4600 for silt soils. An extensive compilation in Ames and Rai (1978) reveals an extremely wide range of values but most are less than 5000. Looney et al., (1987) recommends 500. A value of 5000 is considered conservative.

(5) *Radium* Thibault et al. (1990) gives K_d 36000 for silt soils and 9100 for clay soils, both of which seem excessively high. Other authors, esp. Looney et al. (1987) give vallues less than 1000. A value of 5000 is considered conservative.

(6) *Cadmium* Looney et al. (1987) suggest K_d less than 10 and only indicate a range of 1 to 100. Thiubault et al. (1990) give a maximum of 560 for clay soils and Rai and Zachara

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(1984) cite studies reporting K_ds up to 1000 for montmorillonitic soils. A value of 1000 is considered conservative.

(7) *Beryllium* According to Rai and Zachara (1984) very little is known about Be partitioning but they did report that K_ds appear to be higher than those for Cd. Thibault et al. (1990) give a maximum K_d of 1300 for clay soils. A value of 2000 is considered conservative.

(f) The entire point of this column is to summarize a prediction of the success of the leach test for each analyte. "Success" is defined as the ability to measure credibly the analyte in the final solution and thus calculate an apparent or effective partition coefficient. Roy et al. (1991) describe the importance of and rationalle for selecting soil/water ratios when conducting adsorption batch experiments. However, all their discussions apply to starting conditions where the soil (sorbent) is free of the analyte of concern and known quantities of the analyte are added to the liquid. The starting conditions for the leaching tests proposed here are essentially opposite and require a different approach to predicting their behavior.

Information in this column is derived from attached figures. In all cases the attached plots and the performance of a leaching experiment is predicted from the following equations:

(1) $K_d = \dfrac{C_{i,S,eq}}{C_{i,L,eq}} = \dfrac{M_{i,S,eq}/M_S}{M_{i,L,eq}/V_L}$ where for all cases

(2) $M_{i,S,eq} + M_{i,L,eq} = M_{i,T,eq}$ and upon rearrangement

(3) $M_{i,S,eq} = \dfrac{\left(\dfrac{K_d\, M_S}{V_L}\; M_{i,T,eq}\right)}{\left(1 + \dfrac{K_d M_S}{V_L}\right)}$ and for initial conditions and for the

case where zero i is present in the initial liquid phase,

(4) $M_{i,T,eq} = M_{i,S,int} = C_{i,S,int}\, M_S$ so that

(5) $M_{i,S,eq} = \dfrac{\left(\dfrac{K_d\, M_S^2}{V_L}\; C_{i,S,int}\right)}{\left(1 + \dfrac{K_d M_S}{V_L}\right)}$ and $C_{i,L,eq}$ can then be obtained from (1)

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Main Symbols:

C = concentration or activity (eg. mg/Kg or pCi/Kg for solids and mg/L or pCi/L for liquids)
M = mass (Kg)
Kd = partition coefficient (ml/g or L/Kg)
V = volume (L)

Subscripts:

i = contaminant species
S = soil (solid) phase
L = liquid (aqueous) phase
eq = for equilibrium conditions between soil and liquid
T = total
int = initial conditions

As discussed briefly in (d) above, the equilibrium liquid contaminant concentration for a closed-system leach test ($C_{i,L,eq}$) is very insensitive to soil/liquid ratio $\left(\frac{M_S}{V_L}\right)$ for large values of K_d. Unfortunately large K_ds obviously present the most significant analytical problems because the contaminant is strongly partitioned to the solid phase, not in the liquid phase to be analyzed. The only factor which impact the liquid-phase analyte concentration is the initial concentration in the solid phase - hence the importance of selecting the most contaminated soils for the leach experiments (see (d) above). At lower K_d values the soil/liquid ratio does indeed have a pronounced affect on analyte concentrations in the liquid but in general there is no analytical probelem at low K_d in the first place.

This column lists the maximum K_d value that could be resolved (calculated from the leach experiment results) for each analyte <u>at 10 X the minimum detection limit (MDL)</u> assuming the starting soil concentration given and a mixture of <u>500 g of soil in 2.5 L of liquid (1:5 ratio)</u>. 500 g was selected to allow a representative sample to be used (too small a quantity would increase the chances of non-representation). From Roy et al. (1992) it is apparent that ratios as high as 1:5 are feasible. Also shown are the maximum possible resolvable K_d at the minimum detection limit (MDL).

* These analytes are likely to be problematic, i.e. we may not be able to resolve the highest possible K_d. However, it should be remembered that all estimates are based on "worst case" conditions (with respect to the experimental procedure).

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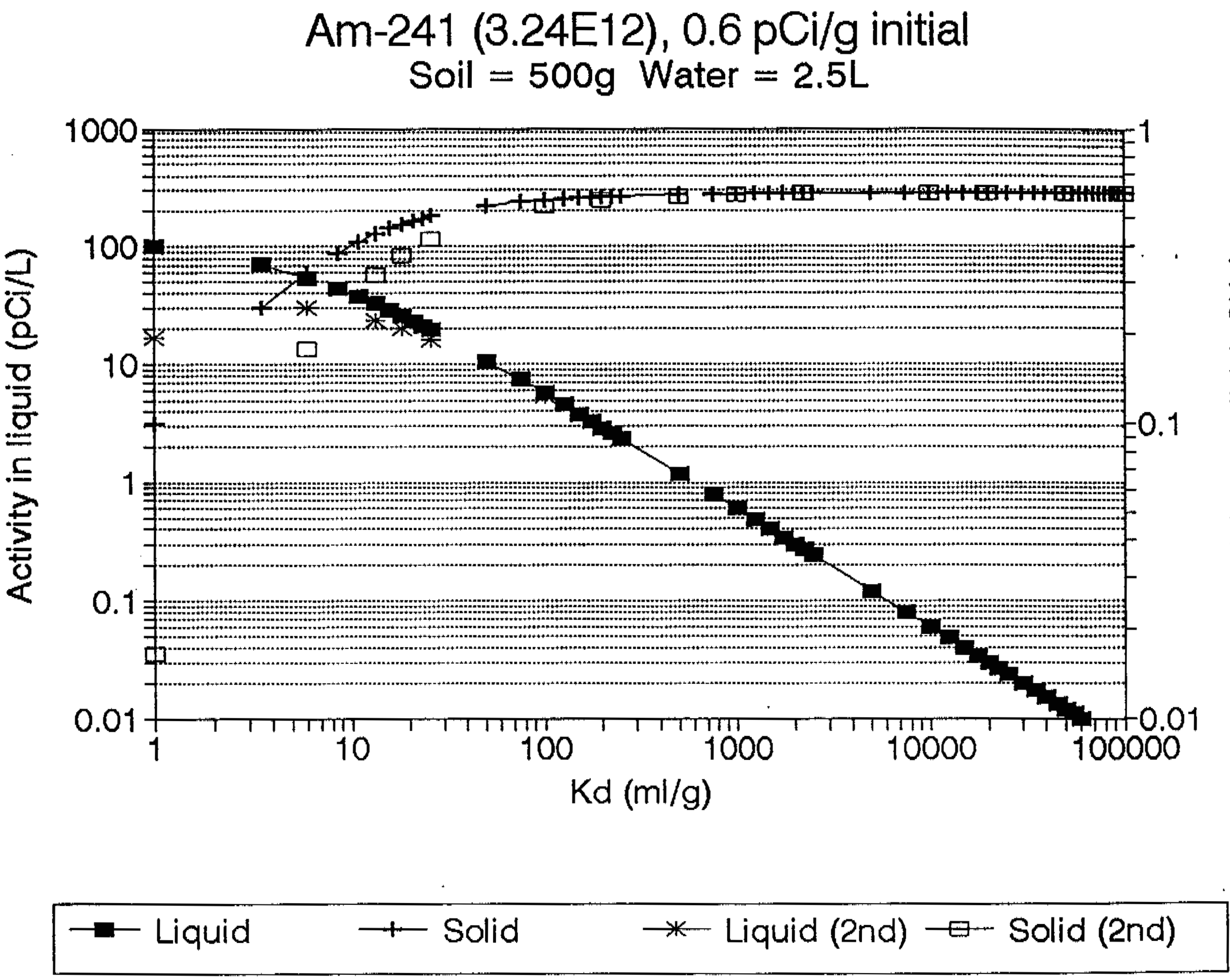
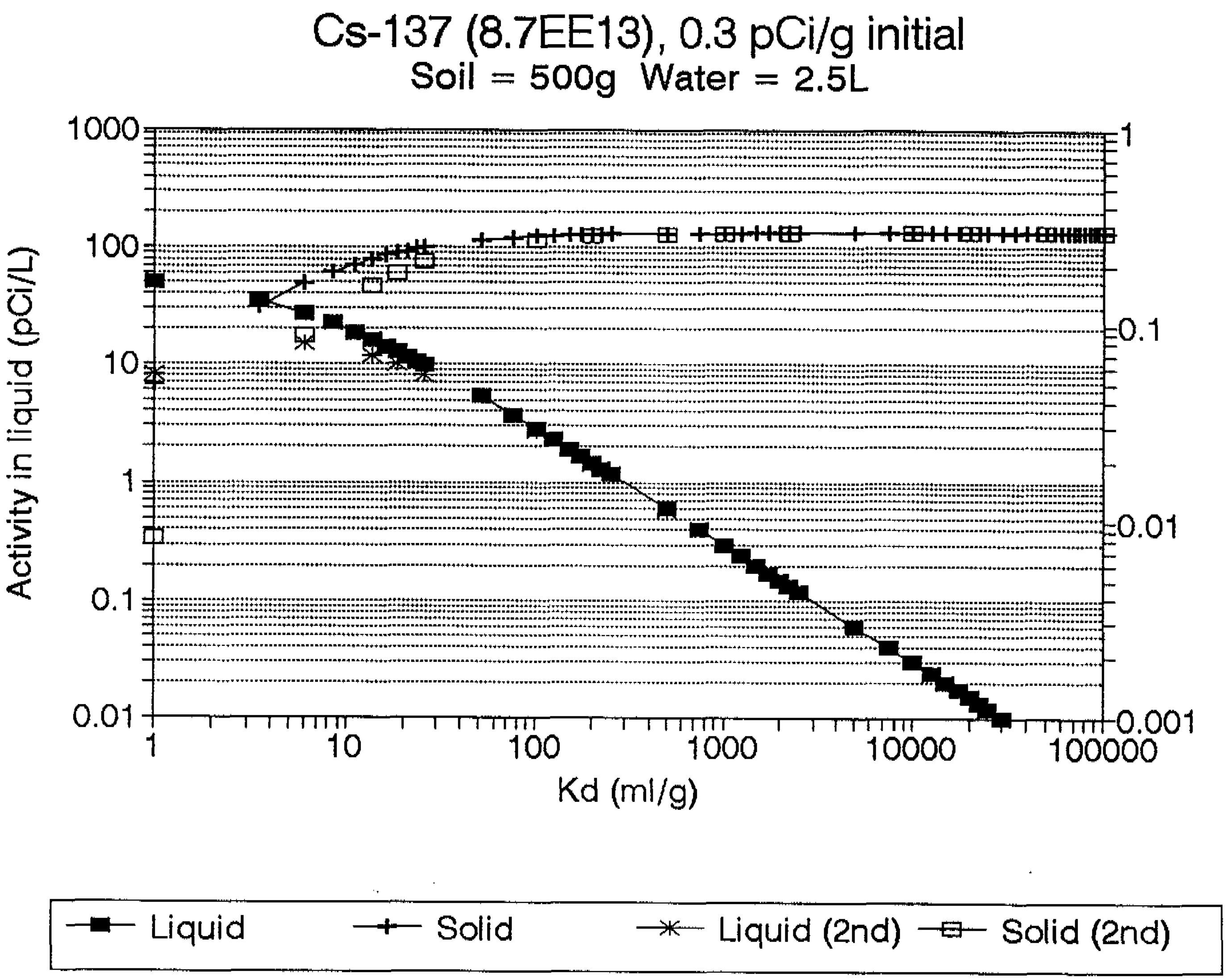


Am-241 (3.24E12), 0.6 pCi/g initial
Soil = 500g Water = 2.5L
Activity in liquid (pCi/L)
Activity in solid (pCi/g)
Kd (ml/g)
1000
100
10
1
0.1
0.01
0.1
0.01
1
10
100
1000
10000
100000
Liquid
Solid
Liquid (2nd)
Solid (2nd)



Cs-137 (8.7EE13), 0.3 pCi/g initial
Soil = 500g Water = 2.5L
1000
100
10
1
0.1
0.01
1
0.1
0.01
0.001
1
10
100
1000
10000
100000
Kd (ml/g)
Activity in liquid (pCi/L)
Activity in solid (pCi/g)
Liquid
Solid
Liquid (2nd)
Solid (2nd)

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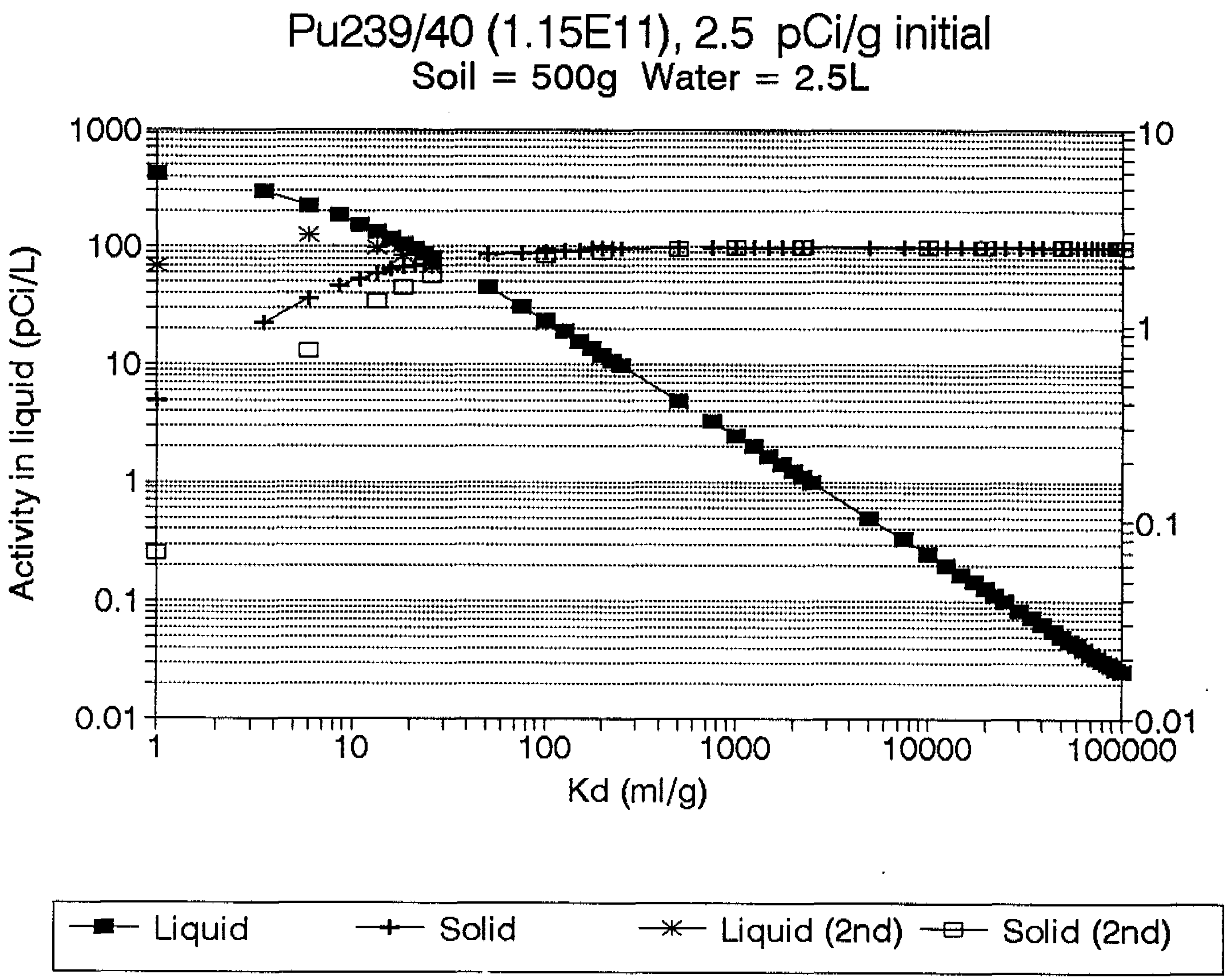

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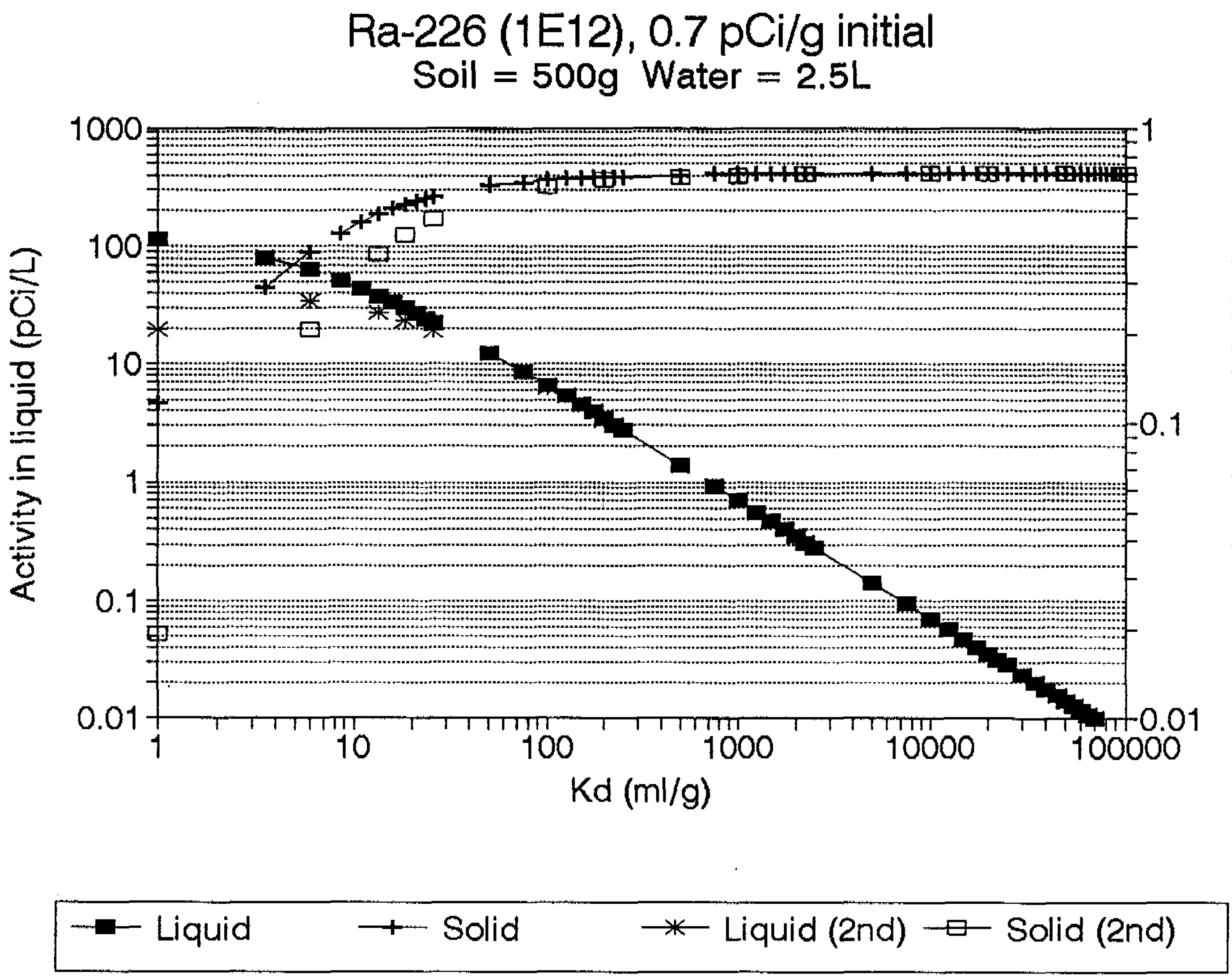

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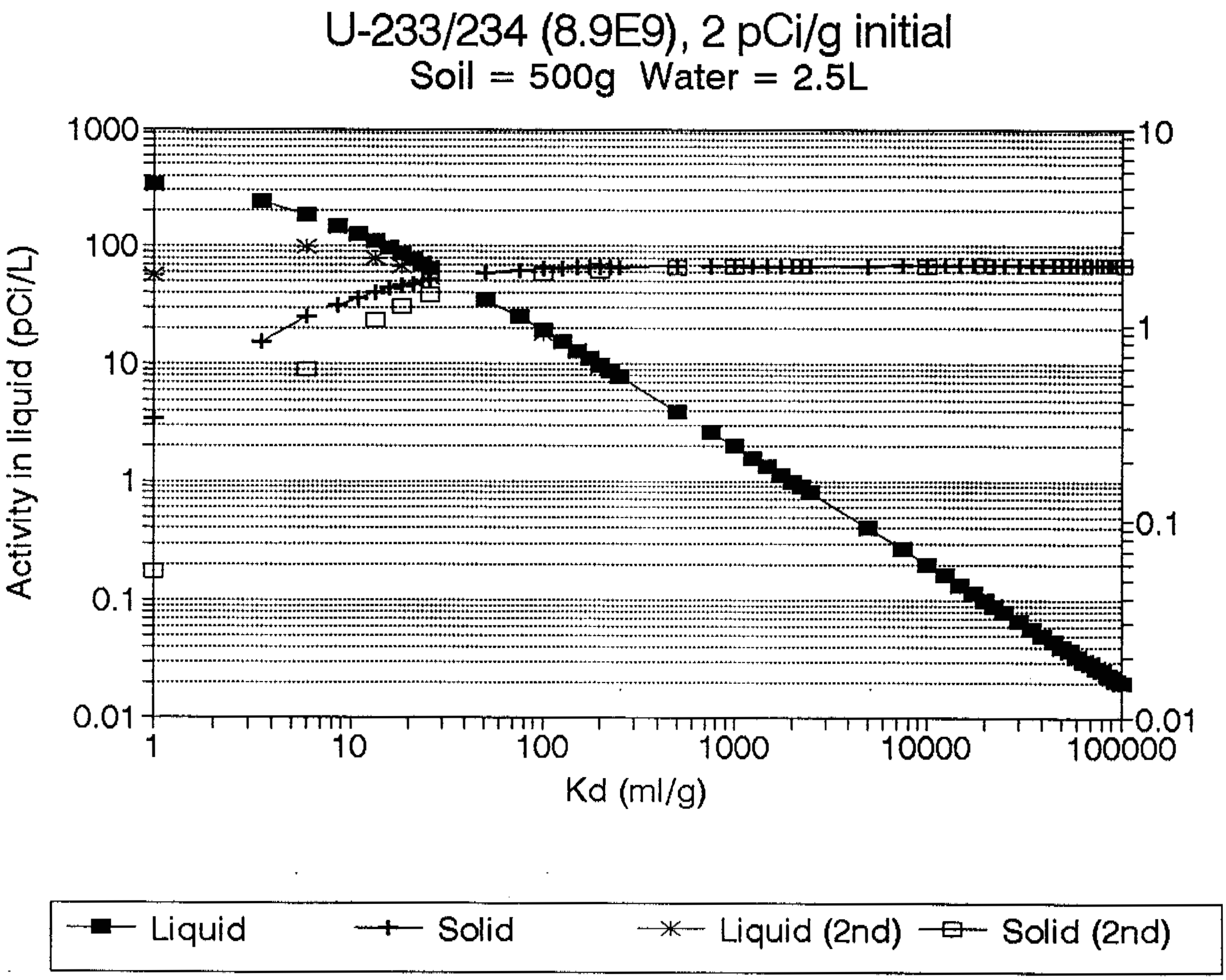
U-233/234 (8.9E9), 2 pCi/g initial
Soil = 500g Water = 2.5L
Activity in liquid (pCi/L)
Activity in solid (pCi/g)
Kd (ml/g)
1000
100
10
1
0.1
0.01
10
1
0.1
0.01
1
10
100
1000
10000
100000
Liquid
Solid
Liquid (2nd)
Solid (2nd)

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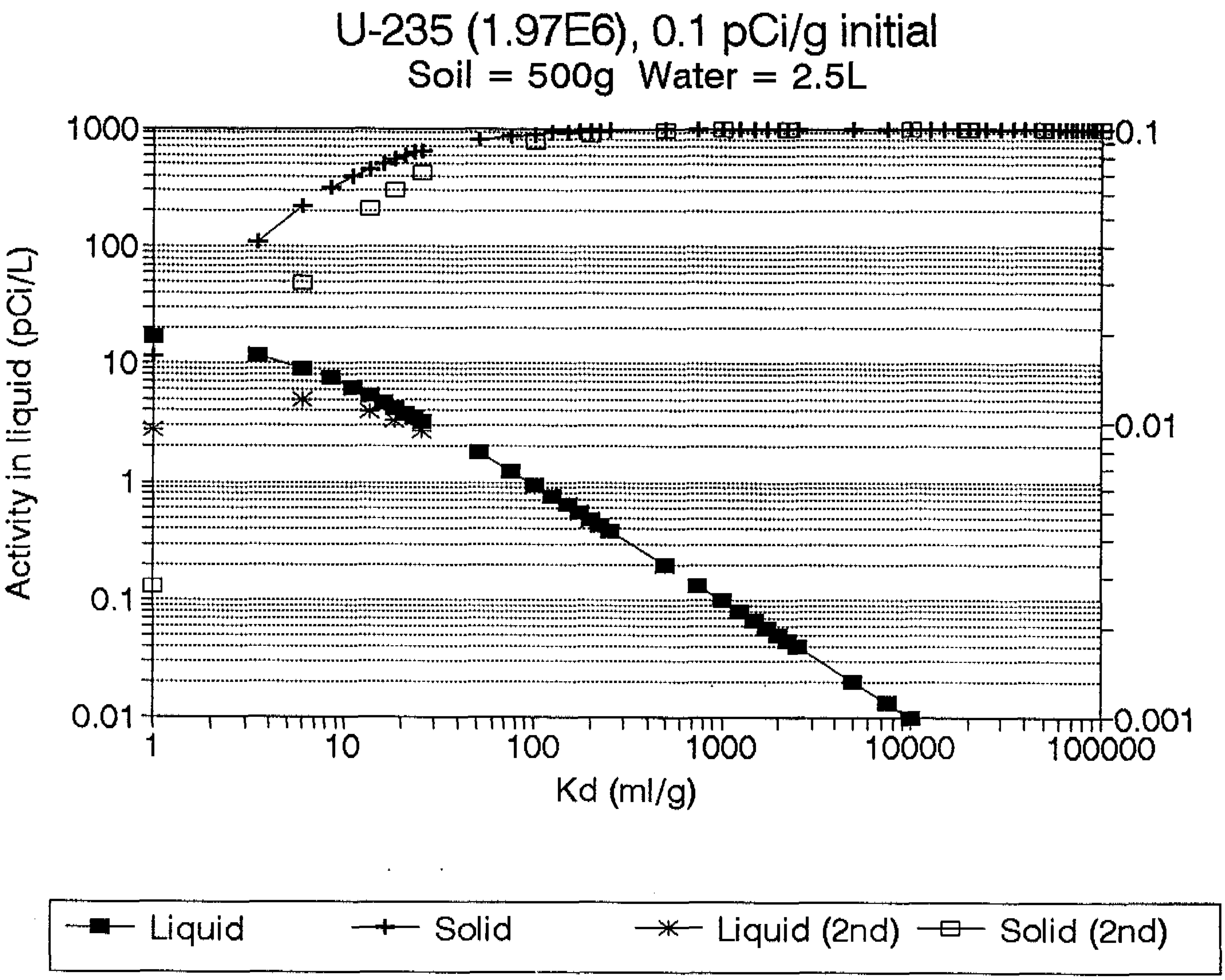

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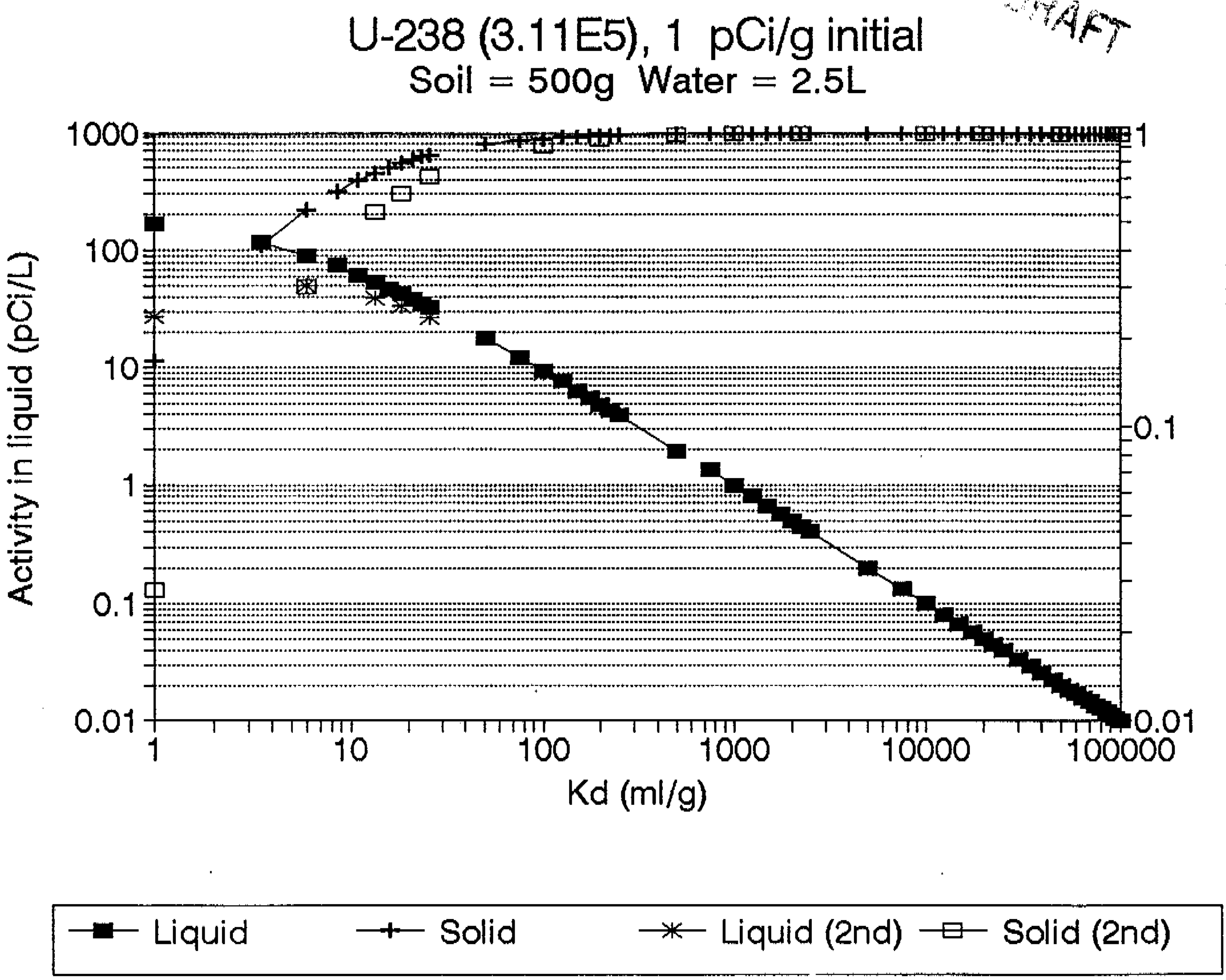

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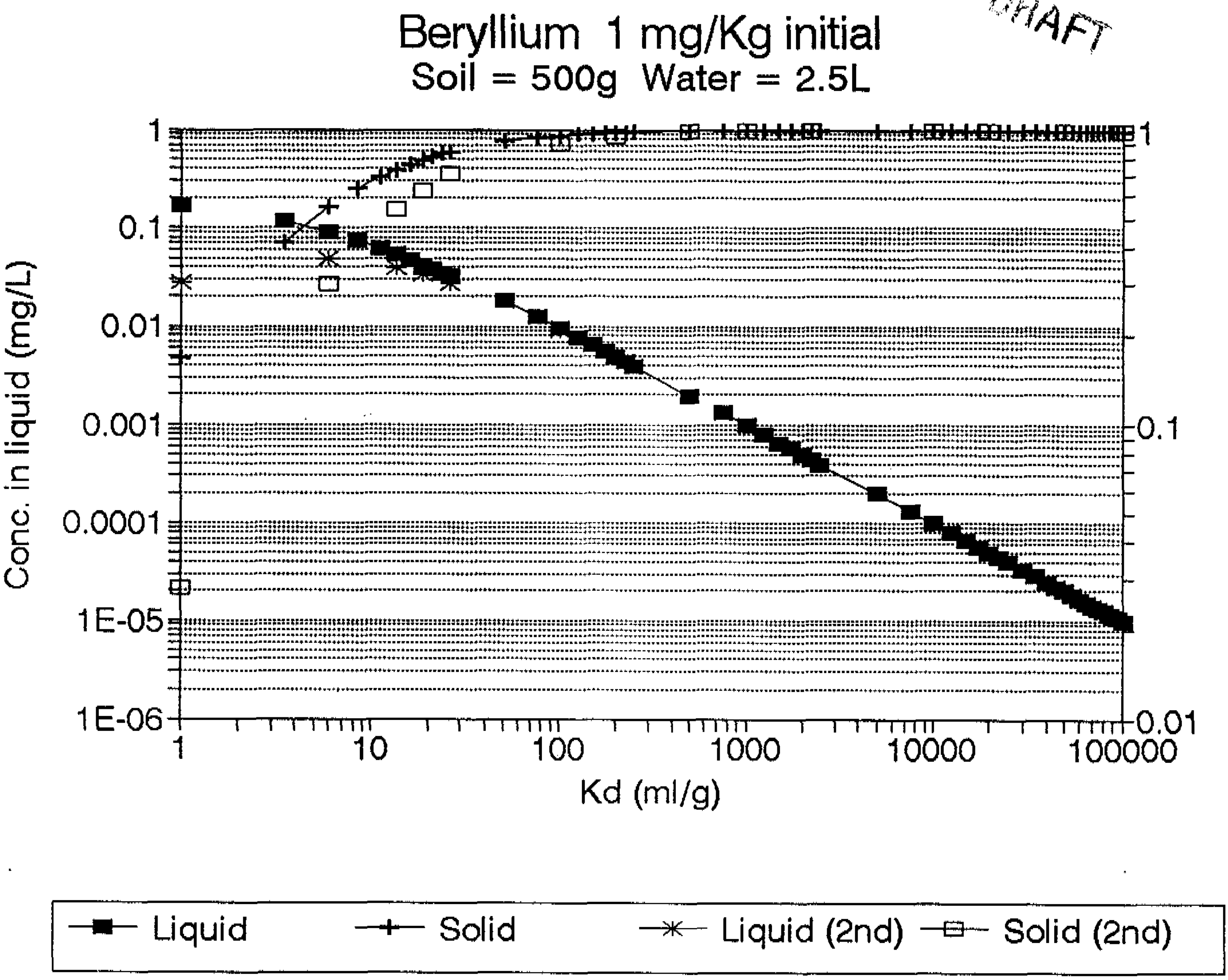

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Cadmium 55 mg/Kg initial

Soil = 500g Water = 2.5L